

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problems Mailbox.**



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁴ : C08G 63/68, A61L 33/00, 27/00	A1	(11) International Publication Number: WO 87/ 03608 (43) International Publication Date: 18 June 1987 (18.06.87)
(21) International Application Number: PCT/EP86/00712 (22) International Filing Date: 5 December 1986 (05.12.86) (31) Priority Application Number: 23112 A/85 (32) Priority Date: 5 December 1985 (05.12.85) (33) Priority Country: IT (71) Applicant (for all designated States except US): AUSIMONT S.P.A. [IT/IT]; 31, Foro Buonaparte, I-20121 Milan (IT). (72) Inventors; and (75) Inventors/Applicants (for US only) : RE, Alberto [IT/IT]; 40, Via Lamarmora, I-20122 Milan (IT). DE GIORGI, Marco [IT/IT]; 1, Via Don Ambrosini, I-21100 Varese (IT). CAPORICCIO, Gerardo [IT/IT]; 13, Via E. Filiberto, I-20149 Milan (IT).	(74) Agent: BARZ, Peter; Schmied-Kowarzik, Weinhold, Barz, Dannenberg, Gudel, Schubert, Siegfriedstrasse 8, D-8000 München 40 (DE). (81) Designated States: DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, NL (European patent), SE (European patent), US. Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: FLUORINATED POLYESTERS (57) Abstract New polyesters comprising polyoxyfluoroalkylene blocks are prepared by polycondensation of diols with dicarboxylic acids or with derivatives thereof, said fluorinated polyesters being characterized by such improved surface properties that any subsequent treatments of the surface of the articles obtained therefrom are needless.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	ML	Mali
AU	Australia	GA	Gabon	MR	Mauritania
BB	Barbados	GB	United Kingdom	MW	Malawi
BE	Belgium	HU	Hungary	NL	Netherlands
BG	Bulgaria	IT	Italy	NO	Norway
BJ	Benin	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland				

Fluorinated Polyesters

- 1 -

1 BACKGROUND OF THE INVENTION

1. Field of the invention

The present invention relates to fluorinated polyesters of the thermoplastic or thermoelastomeric type.

5

2. The Prior Art

There are known thermoplastic polyesters, which are widely utilized as films, fibres, supports for magnetic tapes, structural materials in fields such as the electronic or the biomedical. They are generally prepared by polycondensation of aromatic diacids or their derivatives with diols. Typical examples are polyethyleneterephthalate and polybutyleneterephthalate, which are obtained by polycondensation of terephthalic acid or of a derivative thereof, for example a diester, with ethylene glycol or butandiol, respectively.

15

There are also known thermoelastomeric polyesters obtained by condensation of a diacid or a derivative thereof, such as e.g. a diester, with a low molecular weight glycol and with a polyglycol, generally a polyoxyalkylene glycol having a molecular weight from 1000 to 3000.

20

The thermoplastic and thermoelastomeric polyesters are characterized by high mechanical and electrical characteristics, a good stability to solvents and to hydrolysis.

25

For a plurality of uses such as films, supports for magnetic tapes, fibres, in various sectors of goods, they exhibit however considerable drawbacks, as they have a low oil and water-repellency, a low resistance to soiling and low free flowing properties, characterized by a high friction coefficient, so that a subsequent finishing treatment of such articles is absolutely necessary.

30

In particular, as regards the use for magnetic recording tapes, where the material flows on metal or plastic surfaces, a surface treatment of said surface with a lubricant is required in order to

35

1 reduce friction and to secure the sliding of the tape and preserve
it as much as possible from the wearing. For these uses, very thin
layers on the substrate surface, generally from 50 to 1,000 Å, are
sufficient.

5

For other uses, for example in particular in the biomedical field,
the conventional hydrogenated polyesters, although exhibiting in
comparison with other utilizable materials - improved impermeability
and mechanical properties, do not exhibit good biocompatibility
10 and antithrombogenicity.

With a view to overcoming these drawbacks, the hydrogenated polyesters
are therefore subjected to finishing processes or surface
treatments.

15

These finishing processes or these surface treatments are generally
carried out, for example, with a fluorinated oil or with a
solution or a dispersion of a fluorinated plastic polymer, such
as, for example, a polytetrafluoroethylene dispersion, depending
20 on the type of application. However, these fluorinated coatings
exhibit the drawback of not sufficiently adhering to the substrate,
owing to the surface properties which are typical of the fluorinated
polymer and which interfere with the adhesion. By consequence,
since it is not possible to maintain the fluorinated layer
25 adherent to the article for a sufficiently long period of time, a
degradation of the surface properties occurs, such as resistance
to chemical agents, oil- and water-repellency, resistance to soiling,
free flowing which, conversely, are indispensable for a plurality
of uses.

30

An alternative method of increasing the duration of the abovesaid
surface properties consists in chemically binding a fluorinated
monomer to the polymeric substrate by grafting. This process can
be carried out, for example, by using radiation or electric discharge.
35 charge.

1 With such method, however, the obtaining of a uniform layer is
strictly related to the substrate nature. In fact, on substrates
having an irregular shape no uniform layer of fluorinated coating
can be obtained.

5

According to another method of obtaining fluorinated coatings on
non-fluorinated polyesters, a non-fluorinated polyester is coex=
truded with a fluorinated copolymer, for example a tetrafluoro=
ethylene/hexafluoropropene polymer. This method, however, besides
10 requiring a particularly complex technology, can be rarely used,
as it can be applied only for particular types of articles, for
example fibres.

By consequence, there was the requirement of having available readi=
15 dily processable polyesters which permit to overcome the above=
said problems of finishing or of surface treatment, and at the sa=
me time having the above-cited characteristics of chemical inertia,
mechanical properties, oil- and water-repellency, biocompatibility.

1 THE PRESENT INVENTION

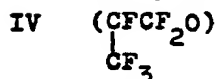
It has now surprisingly been found that polyesters comprising fluoropolyoxyalkylene units represent a novel technological solution which permits to overcome the above-cited limitations as they permit to avoid all surface treatments or finishing operations.

Thus, the object of the present invention is a polyester characterized by a block structure and comprising, with respect to the total number of moles constituting the polyester, amounts not higher than 45% by moles of at least one fluoropolyoxyalkylene comprising the repeating fluoropolyoxyalkylene units selected from the following classes:

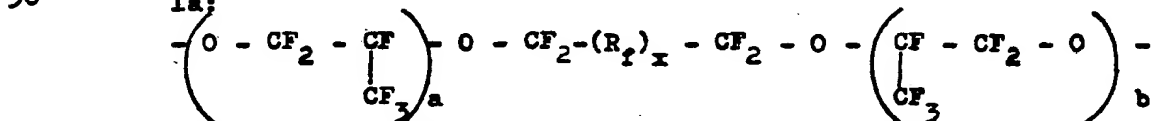
- I (C_2F_4O) , (CF_2O) , said units being randomly distributed along the fluoropolyoxyalkylene chain;
- II (C_3F_6O) , (C_2F_4O) , $(CFXO)$ where $X = -F$ or $-CF_3$, said units being randomly distributed along the perfluoropolyoxyalkylene chain;

III $-CH_2-CF_2-CF_2-O-$ said units being linked to one another inside the fluoropolyoxyalkylene chain as shown by the following structural formula:

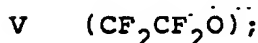
la: $-(O-CF_2-CF_2-CH_2)_p-O-R'_f-O-(CH_2-CF_2-CF_2-O)_q-$ where R'_f is a fluoroalkylene group, preferably containing 1 to 8 carbon atoms, p and q are integers, p+q is at least 2 and, preferably, up to 200;



said units being linked to one another inside the fluoropolyoxyalkylene chain as shown by the following structural formula:



where R_f is a fluoroalkylene group, preferably containing 1 to 8 carbon atoms, x is 0 or 1, a and b are integers and a+b is at least 2 and, preferably, up to 30;



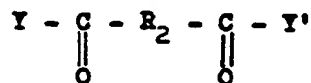
1 VI (CF₂CF₂CF₂O).

5 The fluorinated polyesters of the invention are prepared by directly carrying out a polycondensation of fluoropolyoxyalkylenes comprising the abovesaid repeating units with the cited diols or carboxylic diacids or derivatives thereof. Such fluoropolyoxyalkylenes having functional groups at both ends contain hydroxy end groups or carboxylic end groups and have an average molecular weight of from about 400 to 10,000, the
10 minimum value depending on the type of repeating structure, so that polyesters having a molecular weight equal to at least 20,000 are obtained.

15 The polymers so obtained, besides retaining the excellent properties of the polyesters, particularly mechanical and electrical properties, chemical inertia to common solvents, exhibit also improved surface characteristics, such as oil- and water-repellency, low friction coefficient, chemical inertia to aggressive agents such as hydrocarbon fluids or chlorinated solvents, so avoiding the difficulties connected with the preparation and the carrying out of the fluorinated surface treatment
20 needed for the conventional polyesters. These materials are therefore particularly suitable for a wide variety of uses such as e.g. oil- and water-repellent films and fibres, substrates for magnetic tapes, biocompatible structural materials for biomedical uses.
25

For the preparation of the polyesters of the invention the following compounds are utilized:

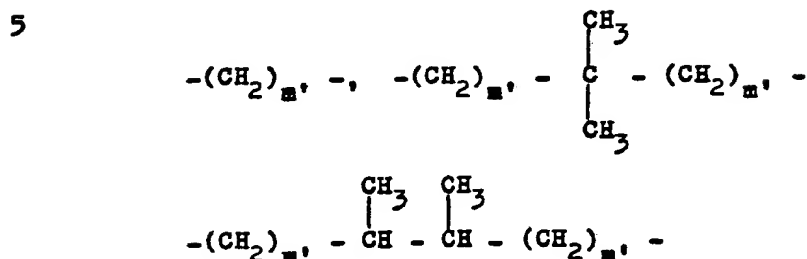
- 30 1) a hydrogenated diacid or diester or diacylchloride having the following general formula:



35 wherein Y and Y', equal or different one another, are halogen or OR', wherein R' is H or an alkyl radical containing from 1 to 8 carbon atoms or an aryl radical having

- 1 fr m 6 to 10 carbon atoms;
 R₂ is a divalent radical having from 2 to 30 carbon atoms such
 as, for example:

a) an alkylene radical of the type:



- 10 wherein m' is an integer from 2 to 20;
- b) a fluorinated or non-fluorinated arylene radical such as
 for example para- or meta-phenylene, para- or meta-xylene;
- c) a cycloaliphatic or polycyclic, fluorinated or non-fluori-
 15 nated, divalent radical, such as for example 1,4-cyclohex-
 xylene, 1,3-cyclohexylene, 2-methyl-1,4-cyclohexylene,
 2-methyl-1,3-cyclohexylene, diarylenmethane, etc.

Particularly suitable for the purposes of the invention are
 the aromatic dicarboxylic acids, such as for example the tereph-
 20 thalic, phthalic and isophthalic acids and their derivatives;

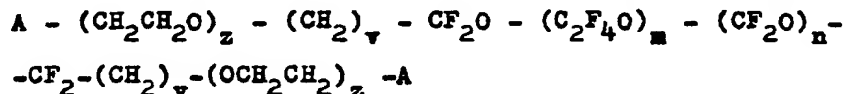
- 2) a hydrogenated diol containing an alkylene radical having from
 2 to 14 carbon atoms, such as ethylene, propylene, tetramethyl-
 ene, hexamethylene, dodecamethylene, cyclohexylene, 2,2-dime-
 thyltrimethylene or cyclohexan-dimethylene;
- 25 3) a difunctional derivative having an average molecular weight
 from about 400 to 10,000, preferably from 500 to 5,000, com-
 prising the fluoropolyoxyalkylene units described above in
 classes I, II, III, IV, V and VI and having end groups of the
 following type:



wherein v and z are integers or zero, preferably v is 0 or 1,
 and z is 0 or an integer up to 3;

1 A is OH, in such case v being at least 1, or COY, Y being the same as defined before.

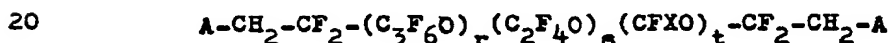
5 Difunctional derivatives having end groups as described before and belonging to class I are particularly selected from those comprised in the following general formula:



10 wherein v, z and A have the meaning defined hereinbefore and m and n are positive integers such that the molecular weight falls within the indicated range.

One can prepare these fluoropolyoxyalkylene derivatives according to known methods, as described for example in
15 patents US 3,810,874 and US 3,847,978.

Difunctional derivatives having the above described end groups and belonging to class II are particularly selected from those comprised in following general formula:



wherein X is -F or -CF₃, indexes r, s, t are positive integers such that the molecular weight is as above indicated, and A is as defined hereinbefore.

25 One can prepare such compounds by photo-oxidation of C₃F₆ and C₂F₄ mixtures, as described in US patent 3,665,041, and by successively converting -COF end groups into groups containing the end group A, such conversion being accomplished according to known methods as described for example in patents US 3,847,978 and US 3,810,874.

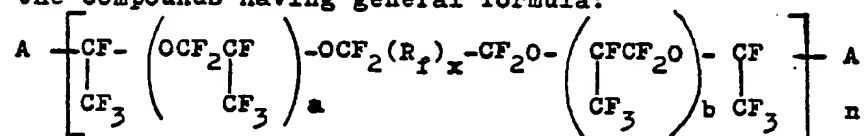
30

Difunctional derivatives having the above described end groups and belonging to class III are particularly selected from the compounds having general formula:

- 1 $A-CF_2CH_2(OCF_2CF_2CH_2)_p-CR'_fO-(CH_2CF_2CF_2O)_qCH_2CF_2-A$
 wherein p, q, A and R'_f are the same as defined hereinabove.

5 These compounds are described in published European patent application 148,482, and the end groups containing -COF can be converted so as to have end groups A, as is described in patents US 3,847,978 and US 3,810,874.

10 Difunctional derivatives having the above cited end groups and belonging to class IV are particularly selected from the compounds having general formula:

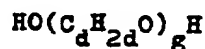


15 where a, b, A, R'_f , x have the meaning defined hereinbefore, n is a positive integer.

Such compounds are described in published European patent application 151,877 and the end groups containing -COF are converted in order to have end groups A as is described in
 20 patents US 3,847,978 and US 3,810,874.

Difunctional derivatives having end groups as described before and belonging to classes V and VI, are prepared by the processes described respectively in US patent 4,523,039 and
 25 European patent application 148,482, both successively followed by the treatments described in Italian patent application 22920 A/85;

- 4) a hydrogenated polyoxyalkylene glycol having an average molecular weight from about 400 to 4,000 and preferably from
 30 1,000 to 2,000, having the following general formula:



where d = 1-4 and g = 6-70, C_dH_{2d} being linear or having side-chains.

- 1 Representative examples of such class of compounds are:
polyethylene glycol, polypropylene glycol, polytetramethyl
ene glycol.
- 5 The fluorinated polyester of the present invention are prepared
by properly mixing the above-specified compounds in such way
that at least one of them is a fluoropolyoxyalkylene derivative
and the molecular weight of the final polyester is not lower
than 20,000.
- 10 According to the present invention, the fluorinated polyesters
comprising the fluoropolyoxyalkylene derivative in amounts not
exceeding 5% by moles, preferably from 0.1 to 5% by moles with
respect to the total number of moles constituting the polyester
15 are particularly suitable for substrates for magnetic tapes, oil-
and water-repellent films and fibres.
- The polyesters of the invention having a content of fluoropoly=
oxyalkylene units higher than 5% by moles are particularly utili=
20 zable in the biomedical field due to their high biocompatibility.
- By properly varying the components from 1) to 4), it is possible
to obtain thermoplastic or thermoelastomeric materials. The
thermoelastomeric materials contain a rubber-like phase which
25 may consist either of fluoropolyoxyalkylene or of polyoxyalkylene
glycol or of mixtures thereof. Generally, in the presence of
high fluoropolyoxyalkylene contents, for example of 30% by moles,
the polyester is thermoelastomeric; in case of lower amounts,
≤ 5% by moles, it is necessary to add polyoxyalkylene glycols.
- 30 One can prepare the polyesters of the invention by conventional
polycondensation techniques, such as for example, in bulk, in
solution, in emulsion, interface polycondensation.
- 35 Always according to the known polyester synthesis methods, the
polycondensation can be carried out starting from dicarboxylic

1 acids and diols, or by transesterification starting from diesters
and diols, or from diacylchlorides and diols.

Particularly suitable for the purposes of the present invention is
5 the transesterification and bulk-polycondensation process starting
from mixtures of diesters and diols.

Such process is accomplished by first heating the mixture of reagents
diesters and diols, in proper molar ratios, in the presence
10 of a catalyst, to a temperature from about 200 to 240°C; in this
step, the distillation of the by-products (alcohols) generated
during the transesterification takes place.

The reaction is carried out in an inert atmosphere, under vigorous
15 stirring and for a time sufficient for the complete removal of the
by-products.

The operation time depends on the monomer type, the temperature,
the catalyst and the excess of diol employed.

20 This process step leads to a low molecular weight prepolymer which
is converted to a polymer having a molecular weight suitable for
high temperature (250-300°C) polycondensation under stirring and
at a residual pressure lower than 1 torr, in order to remove the
25 excess of low molecular weight diol.

The polycondensation time, which is a function of the operative
conditions, generally ranges from 0.5 to 10 hours.

30 It is possible to use different types of catalysts, such as, for
example, salts of divalent and trivalent metals, such as calcium,
manganese, iron, magnesium, aluminium, zinc; oxides of germanium,
lead and antimony; alkaline metals (sodium, potassium) alkoxides,
titanium alkoxides (isopropylate, butylate).

35 Both process steps, i.e. transesterification and polycondensation,

1 ar generally effected in the absence of solvents:
the materials are in the molten state.

5 The polycondensation can be also carried out in solution, using
diacylchlorides and diols.

10 The fluorinated polyesters of the present invention, as mentioned
above, permit to obtain, by suitably varying the starting composition of the mixture, both plastic-type and elastomeric-type materials, each type being characterized by excellent mechanical properties. Those skilled in the art will have no difficulty in determining the best compositions for the various utilizations.

15 The mechanical properties of these fluorinated polyesters, however,
can be modified, according to the requirements and the desired appliances, by adding various inorganic additives known in the art, such as carbon black, silica gel, alumina and glass fibres. For a few uses, in particular, it is advisable to incorporate stabilizers to heat and to ultraviolet radiations, well known in the art.

20 Furthermore, it is possible to obtain polyesters with a different fluorine content by properly varying the initial molar ratio of the fluoropolyoxyalkylene derivative to the other reagents.

25 The fluorinated polyesters obtained according to the present invention have the same fields of use as the analogous non-fluorinated polyesters with the advantage that the articles prepared from said fluorinated polyesters, for example, by injection molding or compression molding processes, exhibit, as compared with the known products, improved properties as regards oil- and water-repellency,
30 self-lubrication, free flowing and biocompatibility.

This properties improvement occurs also for very low amounts, even
of 0.5% by moles, of fluoropolyoxyalkylene compound with respect
35 to the final polyester.

1 A further advantage of the polyesters of the present invention is
the possibility of mixing a thermoplastic or thermoelastomeric po=
lyester having a high fluorine content, according to the invention,
with other fluorinated or non-fluorinated polymeric materials, and
5 of treating the resulting mixture according to a suitable conver=
sion technology. In this way it is possible to have available a
wide range of materials endowed with improved properties in compa=
rison with those obtained from the individual components of the
mixtures.

10

The polyesters of the invention were characterized by determining:
Melting point: thermal differential analysis at a heating rate
of 20°C/minute.

Technological properties:

15

modulus

tensile strength ASTM D 638 and D 412

elongation at break

Shore hardness ASTM D 2240

contact angle: determination by means of a 40 X grazing light
20 microscope

friction coefficient ASTM D 1894-73

water absorption ASTM D 570 - 24 hours.

25

The test-pieces were prepared by compression molding, operating
at temperatures higher by 30-40°C than the polymer melting point,
the polymer having been previously dried at 100°C under vacuum.

The following examples are given for merely illustrative purpo=
ses and are not to be considered as limitative of the invention.

30

EXAMPLE 1

120.6 g (0.62 mols) of dimethyl terephthalate (DMT), 89.4 g
(0.99 mols) of 1,4-butanediol and $1.2 \cdot 10^{-3}$ mols of titanium
tetraisopropylate (in an isopropanol solution) were charged
35 into a three-neck flask having a 0.5-liter volume, equipped with
a stirrer, a dropping funnel and a column for the distillation

1 of the reaction by-products.

Into the dropping funnel there were introduced 62 g (0.031
mols) of α, ω -bis-hydroxy-polyoxyperfluoroalkylene having
5 an average molecular weight equal to 2000 (formula described
at point 3), belonging to class I with $A = OH$; $v = 1$; $z = 1$).

The flask was repeatedly subjected to vacuum and nitrogen-fil-
ling cycles and was subsequently dipped into an oil bath pre-
10 viously heated to 200°C.

The reaction was conducted under stirring and in a nitrogen
atmosphere, and the methanol distillation begun directly after
melting of the mass.

15 After 30 minutes, when the distillation of the theoretical
amount of methanol was concluded, the polyoxyperfluoroalkylene
diol was added and the whole was allowed to react for 1 hour
at 210°C.

20 The bath temperature was then brought to 250°C while the pres-
sure was gradually lowered to 0.1 torr.

Polycondensation was carried out for 2 hours, where-after it
25 was cooled to room temperature while simultaneously introducing
nitrogen into the reaction flask until the atmospheric pressure
was reached.

The fluorinated polyester, having the appearance of a light
30 mass, exhibited the following characteristics:

melting point: 220°C
Fluorine content: 18% by weight
Shore hardness D: 72
tensile strength: 540 kg/cm²
35 elongation at break: 310%.

1 The il- and wat r-rep ll ncy properties and the friction coeffi-
 cient of the fluorinated polyester were compared with those of a
 polybutyleneterephthalate sample (check A).

5	Fluorinated <u>polyester</u>	Check A <u> </u>
	contact angle with H ₂ O	104 55
10	contact angle with ligroin	20 complete wetting
	contact angle with nitromethane	55 36
	dynamic friction coefficient (μ)	
15	on steel	0.15 0.33
	H ₂ O absorption (% by weight)	0.08 0.65

20 EXAMPLE 2

Using the apparatus and the modalities described in example 1, a
 fluorinated thermoelastomeric polyester was prepared, which con-
 sisted of a rigid crystalline phase, a rubber-like amorphous hy-
 25 drogenated phase, an amorphous fluorinated phase having a very
 low Tg.

The reacting mass consisted of DMT (48.5 g, equal to 0.25 mols),
 1,4-butandiol (36 g, equal to 0.4 mols), polyoxytetramethylene
 30 glycol having an average molecular weight equal to 1000 (100 g
 equal to 0.1 mols) and Irganox 1098 ^(R) (1 g) as antioxidant. In
 the second step there was added α , (ω -bis-hydroxy-polyoxyper=
 fluoroalkylene having an average molecular weight equal to 2000
 and having the formula described at point 3), belonging to class
 35 I with A = OH; v = 1; Z = 1 (12.5 g corresponding to 0.00625
 moles). The catalyst is titanium tetraisopropylate (0.1% by

1 moles referred to DMT).

After a 2-hours polycondensation, a high molecular weight fluorinated copolyester was obtained, which exhibited the following properties:

melting point: 194°C

Fluorine content: 4.6% by weight

Shore hardness D: 52

tensile yield strength (25% modulus): 132 kg/cm²

15 tensile strength: 490 kg/cm²

elongation at break: 480%.

20 Analogously with the preceding example, the fluorinated polymer properties were compared with those of a thermoelastomeric copolyether-ester not containing fluorine (check B).

	Fluorinated thermoelastomeric <u>polyester</u>	Check B <u> </u>
25 contact angle with H ₂ O	110	62
contact angle with ligroin	15	complete wetting
30 contact angle with nitromethane	59	39
dynamic friction coefficient (μ) on steel	0.20	0.45

1 EXAMPLE 3

776 g (4 mols) of dimethylterephthalate, 744 g (12 mols) of ethylene glycol, 0.7 g of manganese acetate (II) and 0.7 g
5 of antimony oxide (III) were charged into a glass reactor having a 3 l volume, equipped with a stirrer, a dropping funnel and a column for the distillation of the reaction by-products.

10 Into the dropping funnel there were introduced 80 g (0.04 mols) of α, ω -bis-(methylcarboxylate)-polyoxyperfluoroalkylene having an average molecular weight equal to 2000 (formula described at point 3) belonging to class I, with $A = \text{COOCH}_3$, $v = z = 0$).

15 The reactor was repeatedly subjected to vacuum cycles and was subsequently dipped into an oil bath heated to 180°C.

The mixture was stirred for 2 hours, during which the distillation of methanol took place; after this period of time, the
20 fluorinated diester was added and the whole was allowed to further react for 1 hour.

The bath temperature was then brought to 280°C, while simultaneously and progressively reducing the pressure to 0.1 mm Hg.
25

After a 2-hour polycondensation, during which the distillation of the ethylene glycol in excess occurred, it was cooled to room temperature.

30 The fluorinated polyester (m.p. = 250°C, Fluorine content = 5% by weight), after grinding in a rotary ball mill, was extruded at 290°C by means of a laboratory flat-head extruder, was cooled to 25°C, longitudinally stretched at 95°C to 300%, transversally stretched at 120°C to 300% and subsequently treated at 215°C for
35 a few seconds to give a biaxially oriented film having a thick=

1. n ss of 100 μ m.

The fluorinated polyester film exhibited improved surface properties with respect to a conventional polyethyleneterephthalate
5 film.

In fact, the values of the contact angle with H_2O and of the dynamic friction coefficient on steel were equal to 103° and to 0.25, respectively, in comparison with 70° and 0.55 of a poly-
10 ethyleneterephthalate film not containing fluorine.

1 CLAIMS:

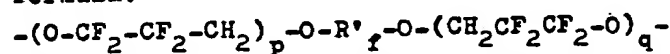
1. A polyester having a block structure and comprising, with respect to the total number of moles constituting the polyester, not more than 45 mole % of at least one fluoropolyoxyalkylene comprising the repeating fluoropolyoxyalkylene units selected from the following classes:

I (C_2F_4O) , (CF_2O) , said units being randomly distributed along the fluoropolyoxyalkylene chain;

II (C_3F_6O) , (C_2F_4O) , $(CFXO)$ with $X = -F$ or $-CF_3$, said units being randomly distributed along the fluoropolyoxyalkylene chain;

III $-CH_2-CF_2-CF_2-O-$

said units being linked to one another inside the fluoropolyoxyalkylene chain as shown by the following structural formula:

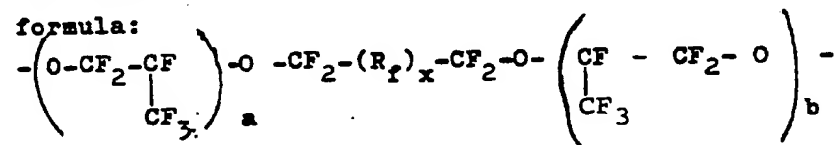


where R'_f is a fluoroalkylene group, p and q are integers, $p+q$ is at least 2;

IV $(CFCF_2O)$



said units being linked to one another inside the fluoropolyoxyalkylene chain as shown by the following structural formula:



where R_f is a fluoroalkylene group, x is 0 or 1, a and b are integers and $a+b$ is at least 2;

V (CF_2CF_2O) ;

VI $(CF_2CF_2CF_2O)$.

1 2. The polyester according to claim 1 prepared by using the following compounds:

1) a hydrogenated diacid or diester or diacylchloride having the following general formula:



wherein Y and Y', equal or different one another, are halogen or OR', wherein R' is H, or an alkyl radical containing from 1 to 8 carbon atoms, or an aryl radical having from 6

10

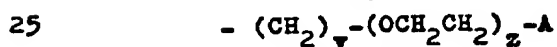
to 10 carbon atoms;
R₂ is a divalent radical having from 2 to 30 carbon atoms, selected from:

- 15
- a) an alkylene radical;
 - b) a fluorinated or non-fluorinated arylene radical;
 - c) a cycloaliphatic or polycyclic, fluorinated or non-fluorinated divalent radical;

2) a hydrogenated diol containing an alkylene radical having from 2 to 14 carbon atoms;

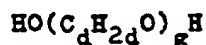
20

3) a difunctional derivative having an average molecular weight from about 400 to 10,000, comprising the fluoropolyoxyalkylene units of classes I, II, III, IV, V and VI of claim 1), and having end groups of the following type:



wherein v and z are integers or zero, A is OH, in such case v being at least 1, or COY, Y being as defined hereinbefore at point 1);

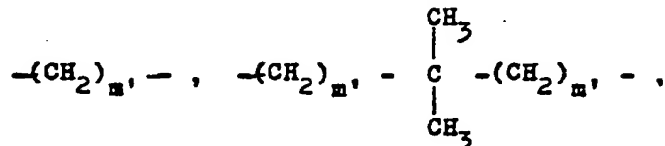
30 4) a hydrogenated polyoxyalkylene glycol having an average molecular weight from about 400 to 4,000, having the following general formula:



where d = 1-4 and g = 6-70, C_dH_{2d} being linear or having side chains.

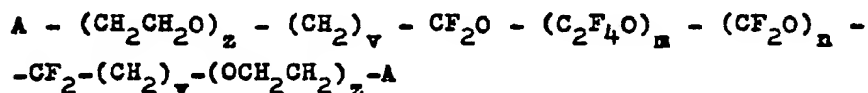
35

- 1 3. The polyester according to claim 2, where in the alkylene radical of point a) is selected from:



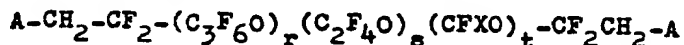
and $-(CH_2)_{m'} - \overset{\overset{CH_3}{|}}{CH} - \overset{\overset{CH_3}{|}}{CH} - (CH_2)_{m'} -$,
wherein m' is an integer from 2 to 20.

- 10 4. The polyester according to claim 2, wherein the arylene radical of point b) is selected from para-phenylene, meta-phenylene, para-xylene and meta-xylene.
- 15 5. The polyester according to claim 2, wherein the divalent radical of point c) is selected from 1,4-cyclohexylene, 1,3-cyclohexylene, 2-methyl-1,4-cyclohexylene, 2-methyl-1,3-cyclohexylene and diarylenmethane.
- 20 6. The polyester according to claim 2, wherein the compound 3) has an average molecular weight from 500 to 5,000.
7. The polyester according to claim 2, wherein the compound 4) has an average molecular weight from 1,000 to 2,000.
- 25 8. The polyester according to claim 2, wherein v is zero or 1 and z is zero or an integer from 1 to 3.
9. The polyester according to claim 2, wherein the compound 1) is an aromatic dicarboxylic acid.
- 30 10. The polyester according to claim 2, wherein the compound 3) has the following general formula:



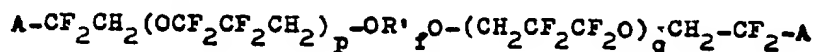
1 wh rein v, z and A have the same meaning as defined in claim
2 and m and n are positive integers such that the molecular
weight falls within the range indicated in claim 2 at point 3).

5 11. The polyester according to claim 2, wherein the compound 3)
has the following general formula:



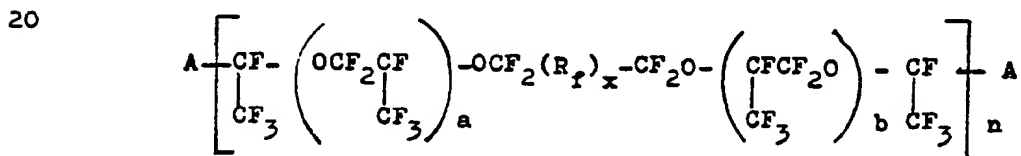
10 where X is -F or -CF₃, the indexes r, s, t are positive inte=
gers such that the molecular weight is that indicated in
claim 2, point 3), and A is the same as defined in claim 2.

12. The polyester according to claim 2, wherein the compound 3)
has the following general formula:



15 where p, q and R'_f are as defined under class III) of claim
1 and A is the same as defined in claim 2.

13. The polyester according to claim 2, wherein the compound 3)
has the following general formula:



25 where a, b, R'_f, x are as defined under class IV) of claim 1,
n is a positive integer and A is the same as defined in claim
2.

14. The polyester according to claim 1, wherein the amount of the
fluoropolyoxyalkylene compound ranges from 0.1 to 5% by mols
with respect to the final polyester.

30

15. Use of the polyester of claim 1 in the biomedical field.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 86/00712

I. CLASSIFICATION F SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁴ : C 08 G 63 /68 A 61 L 33/00, A 61 L 27/00											
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 30%; border-bottom: 1px solid black; padding: 5px;">Classification System</td> <td style="border-bottom: 1px solid black; padding: 5px;">Classification Symbols</td> </tr> <tr> <td style="padding: 5px;">IPC⁴</td> <td style="padding: 5px;">C 08 G; A 61 L</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	IPC ⁴	C 08 G; A 61 L					
Classification System	Classification Symbols										
IPC ⁴	C 08 G; A 61 L										
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black; padding: 5px;">Category ⁹</th> <th style="width: 70%; border-bottom: 1px solid black; padding: 5px;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%; border-bottom: 1px solid black; padding: 5px;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="border: 1px solid black; padding: 5px; vertical-align: top;">X</td> <td style="border: 1px solid black; padding: 5px;">US, A, 3847978 (DARIO SIANESI et al.) 12 November 1974 see claims 1-25; column 8, lines 57-70 cited in the application --</td> <td style="border: 1px solid black; padding: 5px; vertical-align: top; text-align: center;">1-14</td> </tr> <tr> <td style="border: 1px solid black; padding: 5px; vertical-align: top;">A</td> <td style="border: 1px solid black; padding: 5px;">Patents Abstracts of Japan, volume 9, no. 153 (C-288)(1876), 27 June 1985, see the whole abstract & JP, A, 6031535 (KURARAY K.K.) 18 February 1985 -----</td> <td style="border: 1px solid black; padding: 5px; vertical-align: top; text-align: center;">1</td> </tr> </table>			Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X	US, A, 3847978 (DARIO SIANESI et al.) 12 November 1974 see claims 1-25; column 8, lines 57-70 cited in the application --	1-14	A	Patents Abstracts of Japan, volume 9, no. 153 (C-288)(1876), 27 June 1985, see the whole abstract & JP, A, 6031535 (KURARAY K.K.) 18 February 1985 -----	1
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³									
X	US, A, 3847978 (DARIO SIANESI et al.) 12 November 1974 see claims 1-25; column 8, lines 57-70 cited in the application --	1-14									
A	Patents Abstracts of Japan, volume 9, no. 153 (C-288)(1876), 27 June 1985, see the whole abstract & JP, A, 6031535 (KURARAY K.K.) 18 February 1985 -----	1									
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"G" document member of the same patent family</p> </div> </div>											
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="padding: 5px;">10th March 1987</td> <td style="padding: 5px; text-align: center;">15 APR 1987</td> </tr> <tr> <td style="border-bottom: 1px solid black; padding: 5px;">International Searching Authority</td> <td style="border-bottom: 1px solid black; padding: 5px;">Signature of Authorized Officer</td> </tr> <tr> <td style="padding: 5px; text-align: center;">EUROPEAN PATENT OFFICE</td> <td style="padding: 5px;">M. VAN MOL </td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	10th March 1987	15 APR 1987	International Searching Authority	Signature of Authorized Officer	EUROPEAN PATENT OFFICE	M. VAN MOL	
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report										
10th March 1987	15 APR 1987										
International Searching Authority	Signature of Authorized Officer										
EUROPEAN PATENT OFFICE	M. VAN MOL										

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO.

PCT/EP 86/00712 (SA 15440)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 23/03/87

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3847978	12/11/74	None	

For more details about this annex :
see Official Journal of the European Patent Office, No. 12/82